

# Potassium forms in calcareous soils as affected by clay minerals and soil development in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran

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**Abstract:** Potassium (K) is known as one of the essential nutrients for the growth of plant species. The relationship between K and clay minerals can be used to understand the K cycling, and assess the plant uptake and potential of soil K fertility. This study was conducted to analyze the K forms (soluble, exchangeable, non-exchangeable and structural) and the relationship of K forms with clay minerals of calcareous soils in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran. The climate is hotter and drier in the west and south of the province than in the east and north of the province. A total of 54 pedons were dug in the study area and 32 representative pedons were selected. The studied pedons were mostly located on calcareous deposits. The soils in the study area can be classified into 5 orders including Entisols, Inceptisols, Mollisols, Alfisols and Vertisols. The main soil clay minerals in the west and south of the study area were illite, chlorite and palygorskite, whereas they were smectite, vermiculite and illite in the north and east of the province. Due to large amount of smectite and high content of organic carbon in soil surface, the exchangeable K in surface soils was higher than that in subsurface soils. It seems that organic matter plays a more important role than smectite mineral in retaining exchangeable K in the studied soils. Non-exchangeable K exhibited close relationships with clay content, illite, vermiculite and smectite. Although the amount of illite was the same in almost all pedons, amounts of structural and non-exchangeable K were higher in humid regions than in arid and semi-arid regions. This difference may be related to the poor reservoir of K<sup>+</sup> minerals like palygorskite and chlorite together with illite in arid and semi-arid regions. In humid areas, illite was accompanied by vermiculite and smectite as the K<sup>+</sup> reservoir. Moreover, the mean cumulative non-exchangeable K released by CaCl<sub>2</sub> was higher than that released by oxalic acid, which may be due to the high buffering capacity resulting from high carbonates in soils.

**Keywords:** clay minerals; potassium forms; calcareous soils; oxalic acid; K<sup>+</sup> reservoir; Iran

## 1 Introduction

Potassium (K) is known as one of the essential nutrients for the natural growth of plant species (Sparks and Huang, 1985; Islam et al., 2016). The average percentage of K in the Earth's crust is about 2.3%, of which a large quantity is present in the secondary clay minerals. Soil K content could vary based on the type of clay minerals (Mengel and Kirkby, 2001). A large amount of total

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K pools in soils can be caused by the presence of high quantity of K bearing minerals in soils. Muscovite (60–90 g/kg K), biotite (36–80 g/kg K), illite (32–56 g/kg K) and K-feldspars (20–30 g/kg K) are the most important K pools in soils (Mengel, 2006). A long-term non-application of K would cause a large amount of soil K to be depleted (Tan et al., 2017). In arid and semi-arid regions, intensive agriculture without application of K fertilizer could cause a decrease of K in soils, despite a large amounts of K exist in soils (Jalali, 2006). Soil K exists in four forms, including soluble, exchangeable, non-exchangeable and structural forms. Soluble and exchangeable K forms are released rapidly into the soil and are readily available for plants. In addition, a recent study showed that these forms of K are considerably higher in surface soil layer than in subsurface soil layer (Li et al., 2017). There are dynamic equilibrium reactions between different forms of K in soils. The level of soluble K in soils depends on the K depletion by plant uptake, leaching, released K by clay minerals and replacement by other K forms such as exchangeable and non-exchangeable K (Kirkman et al., 1994). The distribution of soil K forms in surface soil layer is distinctly influenced by soil forming processes (i.e., parent materials and soil types) for total K, and mostly influenced by land use changes (i.e., agricultural practices) for exchangeable and available K forms (Blanchet et al., 2017). Exchangeable K is electrostatically retained on the outer surface of clay and humic substances, and is available for plants (Barré et al., 2008). Non-exchangeable K plays an important role in supplying available K, particularly in soils containing K-bearing minerals (Raheb and Heidari, 2012). This form of K is fixed in interlayer of 2:1 clay minerals and could be released gradually (Rees et al., 2013). The composition of parent rocks and soil development stages can determine the amount of structural or mineral K in soils (Sparks and Huang, 1985). The roles of 2:1 clay minerals are very important in soil K cycle. Adsorption and desorption of K have negative correlations with soil buffering capacity and soils with 2:1 clay minerals like illite, vermiculite and smectite (Sparks and Huang, 1985). Soils differ in tendencies to fix the applied K in forms unavailable to plants and each soil has its fixing capacity for K, which must be satisfied before a change in soil solution occurs (Anil et al., 2016). Wood and Schroeder (1991) reported that releasing of non-exchangeable K can be affected by the type of clay minerals. Their results showed that soils containing 2:1 clay minerals release more K than soils with 1:1 clay minerals as dominant clays.

There are lots of researches about the distribution and genesis of clay minerals in soils of Iran as well as in other arid and semi-arid regions in the world (Abtahi, 1980; Ghosh and Singh, 2001; Owliaie et al., 2006; Barré et al., 2008; Anil et al., 2016). The predominant minerals in calcareous soils of Iran are illite, chlorite, kaolinite, palygorskite, smectite and vermiculite, with origins of inheritance, transformation, and neoformation. Due to the high pH values and large amounts of  $\text{Si}^{4+}$  and  $\text{Mg}^{2+}$ , vermiculite is a rare clay mineral, especially in arid and semi-arid regions of Iran (Abtahi, 1980; Khormali and Abtahi, 2003; Owliaie et al., 2006).

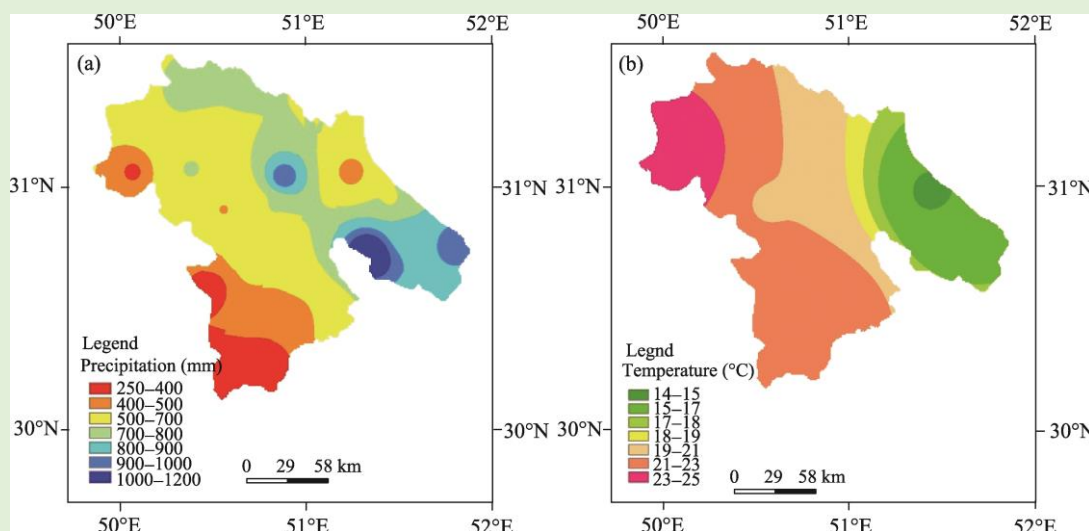
Understanding the soil mineralogy and fertilization background is essential to reduce K loss and obtain high crop production in agricultural lands (Moterle et al., 2016). Though several researches have been done concerning K release and K fixation, there is no sufficient information about K forms and the relationship between K forms and clay minerals, especially in calcareous soils. The relationship between K forms and clay minerals can be used to analyze the K cycling, and assess the plant uptake and potential of soil K fertility. Kohgiluyeh and Boyer-Ahmad Province in Southwest Iran is a region with a large variety of climate and landforms. However, comprehensive investigations about K forms and clay minerals have not been systematically carried out in this region. Thus, this study was conducted to analyze the K forms (soluble, exchangeable, non-exchangeable and structural) and the relationship of K forms with clay minerals of calcareous soils in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran.

## 2 Materials and methods

### 2.1 Study area

This study was conducted in Kohgiluyeh and Boyer-Ahmad Province (30°09'–31°32'N,

49°57'–51°42'E; 500–4409 m a.s.l.), Southwest Iran. It has a land area of  $16.264 \times 10^3 \text{ km}^2$  and contains some intermountain plains within the middle Zagros Mountains. The climate is hotter and drier in the west and south of the province than in the east and north of the province and, therefore, the province is divided into two climatic zones: (1) east region with xeric soil moisture regime and mesic soil temperature regime; and (2) west region with ustic soil moisture regime, and thermic and hyperthermic soil temperature regime. Annual mean temperature ranges from 14 °C to 25 °C and mean annual precipitation ranges from 372 to 830 mm (Fig. 1).



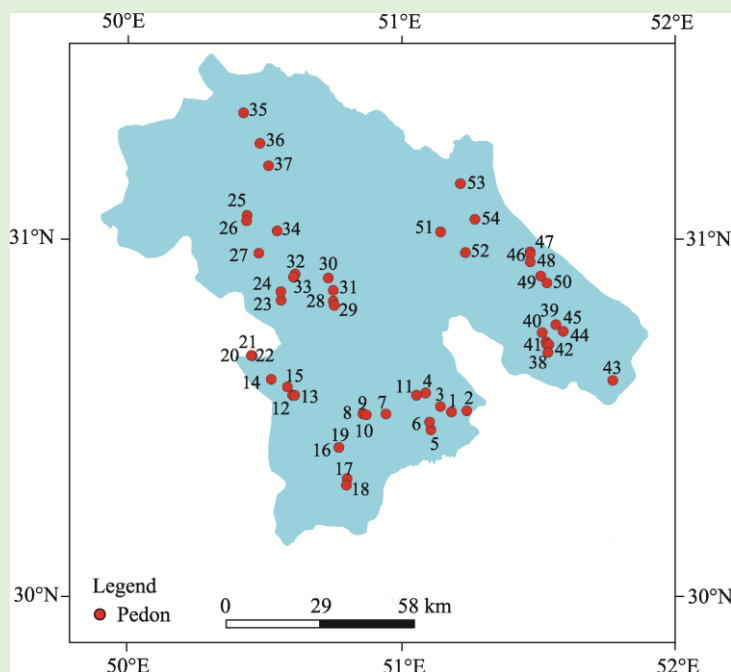
**Fig. 1** Mean annual precipitation (a) and annual mean temperature (b) in Kohgiluyeh and Boyer-Ahmad Province

## 2.2 Soil sampling and analysis

We dug a total of 54 pedons in the study area based on aerial photos, topographic maps and physiographic units, and the distribution of these 54 pedons is shown in Figure 2. We finally selected 32 representative pedons located on calcareous deposits to determine the physical-chemical properties, mineralogical characteristics and different  $\text{K}^+$  forms. We collected 64 soil samples from the 32 representative pedons (in duplicate) according to genetic horizons. The samples were air-dried and then sieved through a mesh size of 2 mm. Soil particle-size distribution was determined using the hydrometer method (Bouyoucos, 1962). Calcium carbonate equivalent (CCE) was measured by neutralization with HCl (Loeppert and Suarez, 1996), and organic carbon (OC) was determined by wet oxidation method (Nelson and Sommers, 1996). Soil pH was measured using the saturated paste extract, electrical conductivity (EC) was measured in soil saturation extract using conductometer, saturation percentage (SP) was determined using the saturated paste extract, cation exchangeable capacity (CEC) was analyzed by replacing exchangeable cations by NaOAc and exchanging  $\text{Na}^+$  with  $\text{NH}_4\text{OAc}$  (Chapman, 1965), and gypsum was measured by precipitation with acetone (Richards, 1954).

Soluble K was measured in the saturated extract, and exchangeable K was extracted by 1.0 M  $\text{NH}_4\text{OAc}$  at pH 7.0 (McLean and Watson, 1985). Non-exchangeable K was extracted by boiling 1.0 M  $\text{HNO}_3$  (Pratt, 1965). Digestion by aqua regia HF method was carried out to determine the total  $\text{K}^+$  (Buckley and Cranston, 1971). For assessing the cumulative non-exchangeable K release with time, we firstly removed the native K with saturation by equilibrating 10 g of soil with 1 M  $\text{CaCl}_2$  three times for 48 h. We then washed out the extra  $\text{Cl}^-$  by alcohol and deionized water. Samples were dried at 65 °C. For each soil sample (64 in total), 2 g of Ca-saturated soil was placed in two centrifuge tubes (in duplicate) with different media including 0.01 M  $\text{CaCl}_2$  and 0.01 M oxalic acid solutions (20 mL in each tube) for 1948 h (2, 4, 8, 14, 24, 36, 48, 72, 96, 144, 192, 268, 436, 604, 940, 1444 and 1948 h) at 25 °C. Subsequently, they were shaken for 1 h before

the suspensions were centrifuged for 10 min. At each stage, the supernatant liquid was determined for K using the flame photometer (Elico Model CL-360, India) (Martin and Sparks, 1983).



**Fig. 2** Locations of the 54 pedons in Kohgiluyeh and Boyer-Ahmad Province

### 2.3 Clay mineralogy analysis

To prepare soil samples for clay mineral analyses, we removed the cementation agents including carbonates, organic matter and iron oxides by 1 N HCl, 30% H<sub>2</sub>O<sub>2</sub>, and dithionite citrate bicarbonate mixed solution, respectively (Mehra and Jackson, 1960; Kittrick and Hope, 1963; Jackson, 1975). Samples containing gypsum were washed with distilled water. After separation of clay fraction, samples were saturated with Mg<sup>2+</sup> and K<sup>+</sup>, using 1 N MgCl<sub>2</sub> and 1 N KCl, respectively. The Mg<sup>2+</sup>- and K<sup>+</sup>-saturated samples were saturated by ethylene glycol and heated at 550 °C, respectively. In addition, samples were treated with 1 N HCl to discriminate kaolinite and Fe chlorite. These five treatments (Mg<sup>2+</sup>-saturated, K<sup>+</sup>-saturated, Mg-ethylene glycol (Mg-EG), K-550 °C and HCL treatments) were analyzed by XRD (X-ray diffraction) diffraction. Relative abundance of clay minerals based on peak intensities was semi-quantitatively measured following the method of Johns et al. (1954).

### 2.4 Data analysis

Soils in the study area were classified according to the U.S. Soil Taxonomy (Soil Survey Staff, 2014). Statistical analyses were performed by Microsoft Excel 2010 and SPSS 19.0.

## 3 Results and discussion

### 3.1 Soil characteristics

Soil classification of the studied pedons according to the U.S. Soil Taxonomy (Soil Survey Staff, 2014) is shown in Table 1. Soils were classified into 5 orders, including Entisols, Inceptisols, Mollisols, Alfisols and Vertisols. Soils with argillic horizon (pedons 38, 42, 44, 45, 49, 51 and 52) were developed mostly in the east and northeast of Kohgiluyeh and Boyer-Ahmad Province with high precipitation, although few developed soils (pedons 2, 7, 23 and 33) were also observed in other regions with low precipitation. The formation of argillic horizon in this region may be due to the process of dealkalization and steppification in the past (Abtahi, 1977). Soils with argillic

**Table 1** Soil characteristics of the studied pedons

Pedon	Horizon	Sand (%)	Silt (%)	Clay (%)	SP (%)	pH	EC (dS/m)	CCE (%)	Gypsum (%)	OC (%)	CEC (cmol/kg)	Taxonomy
1	Ap	27.3	36.0	36.7	48.3	7.9	0.7	44.1	Tr	1.16	15.6	Typic Haplustolls
	Bw1	34.0	30.6	35.4	43.3	7.9	0.8	65.9	Tr	0.67	13.0	
	Bw2	58.0	13.3	28.7	38.7	7.9	0.6	82.2	Tr	0.45	11.1	
	IIC	29.4	17.3	53.3	51.3	8.2	0.4	56.7	Tr	0.47	11.1	
2	Ap	19.3	43.3	37.4	54.2	7.8	0.7	45.4	Tr	1.08	21.7	Calcic Argiustolls
	A/B	17.3	37.3	45.4	50.4	8.0	0.5	40.2	Tr	1.03	18.4	
	Bk1	32.0	33.3	34.7	41.3	8.1	0.4	59.6	Tr	0.74	14.3	
	Bk2	26.9	37.6	35.4	65.2	8.2	0.3	53.9	Tr	0.79	13.3	
	Bk3	27.3	38.0	34.7	45.9	8.2	0.4	55.4	Tr	0.74	12.4	
3	Ap	36.0	36.6	27.4	48.5	7.9	0.6	40.2	Tr	1.59	19.1	Typic Calcustepts
	Bk1	21.3	41.0	37.7	42.8	8.0	0.4	45.4	Tr	1.02	19.8	
	Bk2	25.3	37.0	37.7	44.2	8.1	0.3	42.3	Tr	0.47	14.6	
5	Ap	28.0	44.6	27.4	48.6	7.9	0.7	55.2	Tr	0.96	11.1	Aridic Calcustepts
	Bk1	23.3	42.0	34.7	52.6	8.0	0.3	53.9	Tr	0.51	9.4	
	Bk2	28.0	35.3	36.7	49.9	7.5	0.4	56.7	Tr	0.43	12.4	
7	Ap	46.0	26.6	27.4	34.5	7.9	0.8	60.7	Tr	1.23	13.6	Calcic Haplustalfs
	Btk1	25.3	38.0	36.7	49.2	7.9	0.5	67.8	Tr	0.74	9.4	
	Bk2	32.9	37.6	29.4	43.0	7.8	1.1	65.2	Tr	0.45	9.4	
11	Ap	51.3	27.3	21.4	46.9	7.9	0.7	65.2	Tr	1.34	14.0	Typic Ustifluvents
	C1	46.0	24.6	29.4	36.9	7.7	1.2	62.0	Tr	0.90	14.3	
	C2	59.3	21.3	19.4	32.5	7.9	0.5	74.6	Tr	0.72	12.4	
12	Ap	36.9	39.6	23.4	49.6	7.5	1.6	58.1	1.7	0.52	11.1	Gypsic Haplustepts
	By1	22.0	31.3	46.7	38.8	7.7	1.9	58.3	8.2	0.45	9.4	
	By2	53.3	15.3	31.4	45.3	7.7	1.8	27.0	50.3	0.49	13.3	
	By3	32.0	43.3	24.7	61.6	7.6	1.9	32.0	34.4	0.25	12.2	
13	Ap	37.3	43.3	19.4	35.1	7.6	2.1	64.1	0.4	0.88	7.4	Gypsic Haplustepts
	By	29.3	33.3	37.4	49.3	7.7	0.5	59.4	4.5	0.90	8.8	
	IIC	72.0	17.3	10.7	41.0	7.7	3.7	68.8	15.0	0.54	12.4	
15	Ap	51.3	32.0	16.7	29.7	8.0	0.6	53.3	0.4	0.52	9.1	Gypsic Haplustepts
	C1	53.3	27.3	19.4	36.4	7.6	2.0	80.9	3.2	0.41	7.1	
	C2	51.3	29.3	19.4	34.8	7.5	1.9	67.3	5.1	0.38	9.1	
17	Ap	63.3	25.3	11.4	69.0	7.7	0.8	88.0	0.4	0.87	6.4	Aridic Ustifluvents
	C1	62.0	23.3	14.7	33.2	7.9	0.4	63.8	Tr	0.58	6.4	
	C2	49.3	36.0	14.7	33.8	7.7	0.8	51.2	Tr	0.88	7.0	
21	Ap	17.3	47.3	35.4	55.8	7.3	2.4	61.0	0.5	1.41	11.8	Typic Fluviaquents
	Cg	36.0	33.3	30.7	54.4	7.7	1.4	66.2	Tr	1.05	11.1	
23	Ap	45.3	35.3	19.4	34.2	8.1	0.6	65.2	Tr	0.72	10.5	Calcic Haplxeralfs
	Btk1	23.3	39.3	37.4	51.2	7.9	1.3	67.0	0.5	0.65	12.4	
	Bk2	56.0	16.6	27.4	40.7	8.2	0.3	69.8	Tr	0.43	9.4	
26	Ap	32.0	34.6	33.4	42.7	7.8	0.5	51.3	Tr	1.25	18.4	Calcic Haploxerepts
	Bk1	38.0	31.3	30.7	41.3	7.8	0.4	57.5	Tr	0.92	15.6	
	Bk2	54.0	20.6	25.4	34.5	7.9	0.3	71.7	0.6	0.81	11.1	
29	Ap	32.0	35.3	32.7	43.9	7.8	1.3	62.3	Tr	0.96	17.0	Typic Xerofluvents
	C1	77.3	9.3	13.4	26.2	8.2	0.3	90.7	Tr	0.41	5.5	
	C2	63.3	17.3	19.4	40.1	8.1	0.2	74.9	Tr	0.65	9.4	
30	Ap	36.0	27.3	36.7	42.8	7.9	0.5	70.2	Tr	1.34	16.3	Fluventic Haploxerepts
	Bw1	53.3	10.0	36.7	40.0	8.1	0.3	69.9	0.5	0.60	11.8	
	Bw2	47.3	23.3	29.4	37.3	8.4	0.3	81.7	Tr	0.70	7.7	
33	Ap	17.3	45.3	37.4	45.6	7.6	0.1	41.8	Tr	1.50	17.7	Calcic Haploxeralfs
	Btk1	15.3	32.0	52.7	49.3	7.7	0.8	49.4	Tr	0.70	15.0	
	Bk2	11.3	38.0	50.7	44.3	8.0	1.9	56.0	Tr	0.60	16.3	
	Bk3	22.9	27.6	49.4	42.2	7.7	2.1	59.1	Tr	0.60	12.4	

To be continued

Continued

Pedon	Horizon	Sand (%)	Silt (%)	Clay (%)	SP (%)	pH	EC (dS/m)	CCE (%)	Gypsum (%)	OC (%)	CEC (cmol/kg)	Taxonomy
33	C	24.0	28.6	47.4	46.0	7.9	1.7	56.7	0.5	0.78	13.6	Calcic Haploxeralfs
34	Ap	29.3	39.3	31.4	47.7	7.9	0.4	45.2	Tr	0.90	15.0	Typic Xerorthents
	C1	38.0	27.3	34.7	40.2	7.9	0.3	87.2	Tr	0.78	11.1	
	Cr	27.3	39.3	33.4	37.7	8.2	0.8	83.6	Tr	0.52	11.8	
35	Ap	23.3	32.0	44.7	49.8	7.8	0.4	44.7	0.5	0.79	21.3	Typic Calcixerpts
	Bk1	25.3	27.3	47.4	45.5	8.2	0.3	77.8	0.5	0.56	19.8	
	Bk2	36.0	19.5	44.5	54.5	8.1	0.2	79.9	Tr	0.25	19.1	
36	A	37.3	35.3	37.3	71.1	7.4	1.3	37.3	Tr	5.25	39.0	Typic Haploxerolls
	Bw	37.3	32.0	37.3	47.2	7.9	0.3	54.6	Tr	1.43	22.0	
	C	28.0	37.3	28.0	40.5	8.0	0.3	67.0	Tr	0.60	9.9	
38	Ap	21.3	33.3	45.4	54.3	8.0	0.3	24.9	Tr	0.69	26.7	Pachic Argixerolls
	Bt1	15.3	31.3	53.4	54.4	7.9	0.3	26.8	Tr	0.87	29.2	
	Bt2	19.3	20.0	60.7	71.3	8.3	0.3	24.2	Tr	0.68	33.5	
39	Ap	15.3	39.3	45.4	47.1	7.8	0.6	9.7	Tr	1.14	30.1	Chromic Calcixererts
	Bkss1	16.9	33.6	49.4	27.7	7.8	0.3	17.6	Tr	0.40	30.1	
	Bkss2	17.3	35.3	47.4	56.7	8.2	0.4	18.6	Tr	0.38	25.9	
40	Ap	15.3	42.0	42.7	55.2	7.8	0.5	20.2	Tr	1.26	26.7	Aquic Haploxerepts
	Bg1	17.3	33.3	49.4	64.1	7.8	0.4	17.3	Tr	0.47	31.8	
	Bg2	17.3	38.0	44.7	48.6	8.0	0.4	16.0	Tr	1.21	25.9	
42	Ap	23.3	37.3	39.4	54.6	7.8	0.6	28.1	Tr	2.20	34.4	Mollic Haploxeralfs
	Bt1	23.3	28.0	48.7	53.9	7.8	0.3	31.0	Tr	0.78	32.6	
	Bt2	44.9	19.6	35.4	49.4	7.9	0.3	44.7	Tr	0.49	25.1	
44	Ap	32.0	22.6	45.4	57.9	7.9	0.6	42.8	Tr	1.91	26.7	Mollic Haploxeralfs
	Bt1	14.9	33.6	51.4	57.4	8.0	0.3	43.9	Tr	0.61	22.8	
	Bt2	12.9	33.6	53.4	52.4	8.0	0.3	42.8	Tr	0.68	23.6	
	B	19.3	33.3	47.4	52.2	8.2	0.3	35.5	Tr	0.81	19.8	
45	Ap	17.3	44.0	38.7	60.6	7.7	0.5	52.0	Tr	1.64	24.4	Calcic Haploxeralfs
	Btk1	9.3	35.3	55.4	57.3	8.0	0.3	55.2	Tr	0.76	21.3	
	Btk2	12.9	31.6	55.4	52.9	8.3	0.3	53.1	Tr	0.61	19.1	
46	Ap	35.3	30.0	34.7	57.6	7.7	0.1	48.1	Tr	3.11	25.9	Typic Haploxerolls
	C1	45.3	23.3	31.4	51.2	7.9	0.2	45.4	Tr	0.79	25.1	
	C2	84.0	4.6	11.4	49.7	7.6	0.5	58.4	Tr	0.54	5.3	
47	Ap	56.9	19.6	23.4	34.0	8.0	0.6	65.9	Tr	0.65	9.9	Typic Xerorthents
	C	58.0	19.3	22.7	32.3	8.0	0.6	67.8	Tr	0.51	9.4	
49	Ap	32.0	32.6	35.4	34.4	8.0	0.7	32.3	Tr	2.27	25.1	Calcic Haploxeralfs
	Bt1	25.3	33.3	41.4	48.4	8.1	0.3	59.6	Tr	0.65	18.4	
	Bt2k	27.3	29.3	43.4	40.5	7.6	0.3	35.5	Tr	0.78	22.8	
51	Ap	15.3	38.0	46.7	51.5	8.0	0.2	20.2	Tr	0.88	30.1	Mollic Haploxeralfs
	Bt1	11.3	31.3	57.4	36.1	7.8	0.3	8.1	Tr	1.16	35.3	
	Bt2	21.3	28.0	50.7	39.1	8.2	0.6	29.7	Tr	0.52	23.6	
52	Ap	35.3	39.3	25.4	53.6	7.8	0.5	47.8	Tr	1.16	25.1	Calcic Haploxeralfs
	Btk	23.3	26.0	50.7	40.3	8.0	0.4	41.2	Tr	0.14	24.4	
	Ck	34.9	21.6	43.4	43.2	8.2	0.2	45.4	Tr	0.14	18.4	
53	A	39.3	26.0	34.7	40.7	7.9	2.1	22.6	Tr	1.37	21.3	Typic Xerorthents
	C1	78.0	8.6	13.4	50.9	7.6	1.0	82.8	Tr	0.20	5.5	
	C2	83.3	8.0	8.7	22.5	7.4	1.6	79.6	Tr	0.20	3.5	
54	Ap	12.0	36.6	51.4	58.8	7.9	0.5	47.3	Tr	1.03	16.3	Typic Xerorthents
	C	57.3	20.0	22.7	50.0	7.6	0.8	57.0	Tr	0.85	10.5	

Note: SP, saturation percentage; EC, electrical conductivity; CCE: calcium carbonate equivalent; OC, organic carbon; CEC, cation exchangeable capacity; Tr, trace. A, surface horizon; B, subsoil; C, substratum; A/B, transitional horizon; k, accumulation of secondary carbonates; p, tillage or other disturbance; w, development of color or structure; y, accumulation of gypsum; t, accumulation of silicate clay; g, strong gleying; r, weathered or soft bedrock; ss, presence of slickensides; II, lithologic discontinuities. Numerical suffixes (i.e., 1, 2, 3) are used to denote subdivisions within a master horizon (e.g., Bk1, Bk2).



horizon were classified into Calcic Haplustalfs, Calcic Haploxeralfs, Mollic Haploxeralfs, Calcic Argiustolls and Pachic Argixerolls. The forming processes of these soils mainly occur in piedmont plains and plateaus. Due to high precipitation, these soils are less calcareous, especially in the east and northeast of the province. Because of highly calcareous parent materials and low precipitation in the west and south of the study area, the main horizon is calcic, with accumulation of nodules and powdery pockets of carbonate (pedons 2, 3, 5, 7, 23, 26, 33 and 35 in the western and southern regions and pedons 49 and 52 in the eastern region). Gypsic horizon was found only in the driest area near Gachsaran geological formation (formation with high gypsum content), such as pedons 12, 13 and 15. Cambic horizon was seen as the ordinary horizon in poor developed soils like Inceptisols (Pedin 30) and Mollisols (pedons 1 and 36). Ochric epipedon occurred in all soils of the study area with an exception of Mollisols. Mollic epipedon in pedons 1, 2, 36, 38, and 46 had high OC content and developed structure. Entisols are soils without developed horizon that have been spread in alluvial plains and alluvial fans in all regions.

Most of the soils were loamy with heavy texture, especially Alfisols, while almost all Entisols contained more sand and were coarse-textured. All soils except those pedons (pedons 38, 39, 40, 42 and 51) that occurred in the region with high precipitation were highly calcareous with average calcium carbonate ( $\text{CaCO}_3$ ) content being higher than 40%. Since the variation in CEC of soils is mostly related to the content and type of clay and OC, as a result of increasing in precipitation and weathering in soils in the east and north of Kohgiluyeh and Boyer-Ahmad Province, CEC was higher in these regions than in other regions. According to the results, there was no difference in OC content between humid and arid regions. The OC content was reduced in more humid areas mainly due to intensive agriculture. In addition, the value of EC was low in almost all soils with an exception of gypsic soil.

### 3.2 Soil mineralogy

Relative abundance of clay fractions in the studied soils is shown in Table 2. Smectite, chlorite, illite, palygorskite, vermiculite, kaolinite and interstratified illite-smectite were the dominant clay minerals in the clay samples. The main clay minerals were illite, chlorite and palygorskite in the west and south of Kohgiluyeh and Boyer-Ahmad Province, whereas they were smectite, vermiculite and illite in the north and east of the province. Although illite and chlorite were found in almost all surface and subsurface pedons, they were the major clay minerals in low developed pedons of steep relief, alluvial deposit and regions with low precipitation. In almost all pedons (except some Entisols), illite mineral showed a decreasing trend with increasing depth, mostly due to the enriched sources of illite from the surrounding areas. Because of the inheritance origin and transportation of illite by erosion and aeolian to surface soils, and also the alteration from biotite in surface soils due to daily and seasonal variations in moisture and temperature, illite decreased with increasing soil depth (Khormali and Abtahi, 2003). Alteration of illite to smectite occurred mostly in surface soils of Alfisols and other soils in humid regions, and since smectite was present in fine fraction, therefore contrary to illite, it moved and deposited into the subsurface horizon. Chlorite showed an independent behavior with soil depth and climate. Illite and chlorite are of hereditary origin. Kaolinite occurred in tropical conditions and its origin in the study area was inherited from the surrounding formations and sediments. Except for pedons 12, 13, 15, 17, 46, 47 and 49 which were derived from Gachsaran formation (the most important cap rock of hydrocarbon reservoir in Iran and has important deposits of salt, sulfur and gypsum), other pedons have shown some kaolinite in their clay fraction.

Owliaie et al. (2006) reported that the presence of illite, chlorite and kaolinite in some calcareous soils of Iran has an inherited origin. Smectite was the main clay mineral in the north and east of Kohgiluyeh and Boyer-Ahmad Province, and also in some pedons in the northwest. Since all pedons (with an exception of Pedon 40) were well drained, therefore transformation should be the main process for smectite formation. Sufficient precipitation, especially in the north and east, caused a release of K from illite, therefore the high soil pH and abundance of Mg resulted in the formation of smectite. In addition, some areas have long winters (high precipitation and moderate temperature), as a result, neof ormation also occurred in soils. In some pedons of

arid and semi-arid regions, near the formations with marl parent materials, detrital origin is the dominant reason for the presence of smectite. Khormali and Abtahi (2003) revealed that soil available moisture is the most important factor that determines the distribution of smectite and palygorskite in arid and semi-arid regions.

**Table 2** Semi-quantitative analysis of soil clay content in the studied pedons

Pedon	Soil sample No.	Horizon	Sme	Ill	Chl	Ver	Kao	Pal	Mixed layer
1	1	Ap	+++	+++	++	+	+	++	+ Ill-Sme
	2	Bw1	+++	++	++	+	+	++	+ Ill-Sme
2	3	Ap	+++	+++	++	+	+	++	++ Ill-Sme
	4	A/B	+++	++	+++	+	+	++	++ Ill-Sme
3	5	Ap	+++	+++	+	+	+	++	+ Ill-Sme
	6	Bk1	++	++	+	+	+	++	+ Ill-Sme
5	7	Ap	+++	+++	+	+	+	++	—
	8	Bk1	++	+++	+	+	+	++	—
7	9	Ap	+++	+++	++	+	++	++	—
	10	Btk1	+++	++	+	+	++	++	—
11	11	Ap	++	++	++	+	++	+	—
	12	C1	++	+++	++	+	++	++	—
12	13	Ap	+	++	+++	—	—	+++	—
	14	By1	+	++	++	—	—	++++	—
13	15	Ap	+	+++	++	—	—	+++	—
	16	By	+	++	++	—	—	++++	—
15	17	Ap	++	+++	++	—	—	+++	—
	18	C1	++	++	++	—	—	++++	—
17	19	Ap	++	+++	++	—	—	+++	—
	20	C1	++	++	++	—	—	++++	—
21	21	A	+++	++	++	—	+	++	—
	22	Cg	++	++	++	—	+	+++	—
23	23	Ap	+++	+++	++	—	+	+++	—
	24	Btk1	+++	++	—	—	+	++++	—
26	25	Ap	+++	++	—	—	+	+	—
	26	Bk1	+++	+	—	—	+	+	—
29	27	Ap	+++	+	++	+	+	+	—
	28	C1	+	++	++	—	++	++	—
30	29	Ap	+++	+	—	++	+	+	—
	30	Bw1	+++	+	—	++	+	++	—
33	31	Ap	+++	++	++	+	+	++	—
	32	Btk1	+++	+	++	—	+	++	—
34	33	Ap	++++	+	—	—	+	+	—
	34	C1	++++	+	+	+	+	+	—
35	35	Ap	+++	++	—	+	+	+	++ Ill-Sme
	36	Bk1	++++	+	—	—	+	+	+ Ill-Sme
36	37	Ap	+++	++	++	+	++	—	—
	38	Bw	+++	++	++	—	++	—	—
38	39	Ap	++++	++	+	++	+	—	—
	40	Bt1	++++	+	—	++	+	—	—
39	41	Ap	+++	++	+	++	+	—	++ Ill-Sme
	42	Bkss	+++	+	++	+	++	—	—

To be continued



Continued

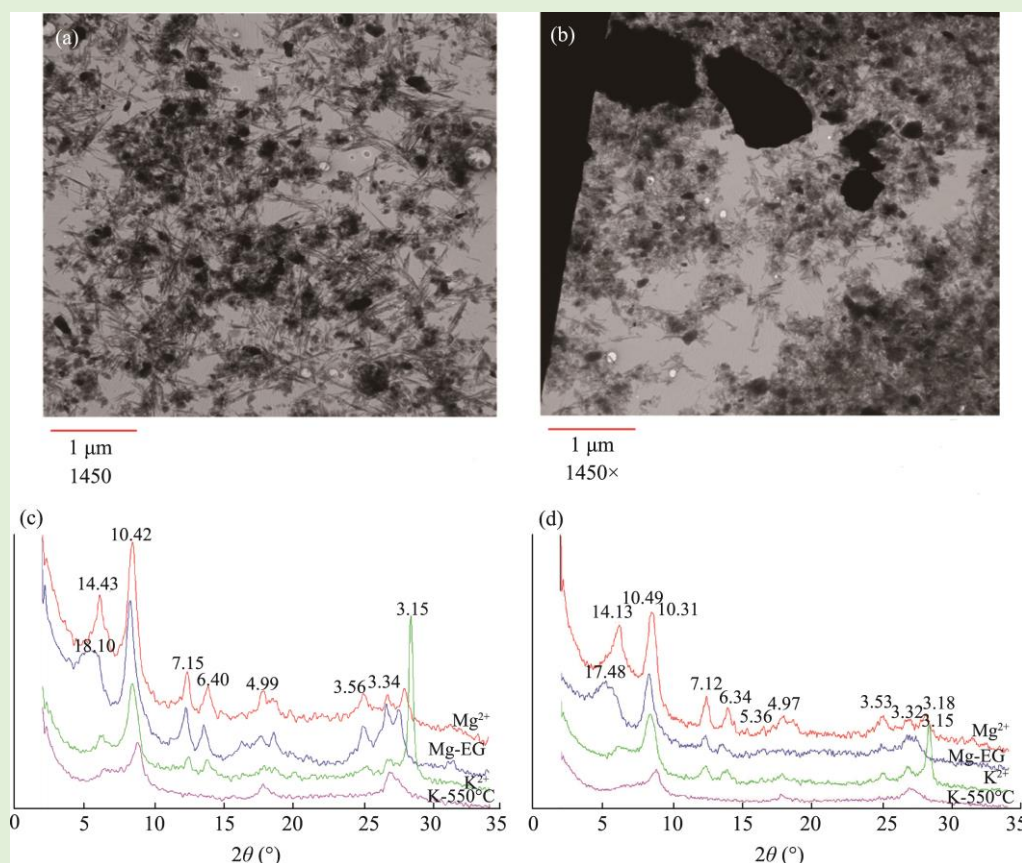
Pedon	Soil sample No.	Horizon	Sme	Ill	Chl	Ver	Kao	Pal	Mixed layer
40	43	Ap	++++	+	+	+	++	+	++ Ill-Sme
	44	Bgl	++++	–	–	+	++	–	++ Ill-Sme
42	45	Ap	+++	+	+	+++	+	–	+ Ill-Sme
	46	Bt1	++++	+	+	++	+	–	+ Ill-Sme
44	47	Ap	++++	–	–	++	+	–	+ Ill-Sme
	48	Bt1	++++	–	–	++	+	–	–
45	49	Ap	++++	+	+	++	++	–	+ Ill-Sme
	50	Btk1	++++	–	–	++	+	–	++ Ill-Sme
46	51	Ap	+++	++	++	++	–	++	+ Ill-Sme
	52	C1	++	++	+++	++	–	–	+ Ill-Sme
47	53	Ap	+++	++	++	++	–	+	–
	54	C	+++	++	++	+	–	++	–
49	55	Ap	++	+++	+++	++	–	–	–
	56	Bt1	++	+	++++	+	–	++	–
51	57	Ap	++++	+++	–	++	++	–	–
	58	Bt1	+++	++	–	+++	+	–	–
52	59	Ap	+++	++	–	++	+	++	–
	60	Btk	++++	+	–	++	+	+	–
53	61	A	+++	+	+++	–	++	+	–
	62	C1	++	++	+++	+	++	++	–
54	63	Ap	++	+++	+	+	+	+++	–
	64	C	+	+++	++	–	+	++	–

Note: Sme, smectite; Ill, illite; Chl, chlorite; Ver, vermiculite; Kao, kaolinite; Pal, palygorskite; Ill-Sme, illite-smectite; –, trace or not detected; +, content <15%; ++, content in the range of 15%–30%; +++, content in the range of 30%–50%; +++++, content >50%.

In arid and semi-arid regions, there was a correlation between smectite and palygorskite with respect to soil available moisture. Vermiculite is a rare clay mineral in the study area. Considering the fact that the acidity of soils in the study area is more than 7 and aluminum is not soluble in these soils, as well as high levels of Mg in the soil solution, we therefore conclude that vermiculite is less stable in the study area. Palygorskite was the dominant clay in arid and semi-arid regions. The main mineral in Gypsic horizon and almost all pedons with calcic horizon was palygorskite (Fig. 3). High specific surface area and high Mg content were the most important properties for this fibrous mineral. Inherence from parent materials and pedogenic formation were the two origins for the existence of palygorskite in the study area. Pedogenic palygorskite can originate from *in situ* transformation of other minerals such as smectite in arid and semi-arid regions (Khormali and Abtahi, 2003) or from authigenic formation of soil solution (Xie et al., 2013). Parent rocks and deposit by water and wind erosion can add palygorskite to soils in regions lacking normal conditions for palygorskite formation (Khademi and Mermut, 1998).

### 3.3 Potassium (K) forms

Amounts of different K forms (soluble, exchangeable, non-exchangeable and structural) in surface and subsurface soils are shown in Table 3. As can be seen, soluble K varied from 0.4 to 36.0 mg/kg (average of 4.2 mg/kg) in surface soils and 0.2 to 11.0 mg/kg (average of 1.8 mg/kg) in subsurface soils. Exchangeable K ranged from 98 to 709 mg/kg (average of 211 mg/kg) and 27 to 438 mg/kg (average of 129 mg/kg) in surface and subsurface soils, respectively. Non-exchangeable K was in the range of 230–956 mg/kg (average of 418 mg/kg) in surface soils and 80–892 mg/kg (average of 295 mg/kg) in subsurface soils. Amounts of structural K varied from 3458 to 9108 mg/kg (average of 5723 mg/kg) in surface soils and 1993 to 10,494 mg/kg (average of 5507 mg/kg) in subsurface soils. Correlation coefficients between soil K forms



**Fig. 3** TEM (Transmission electron microscope) images of clay in (a) By horizon of Pedon 14 and (b) Bk horizon of Pedon 23 showing palygorskite fibres, and XRD (X-ray diffraction) patterns of clay in (c) By horizon of Pedon 14 and (d) Bk horizon of Pedon 23. B, subsoil; y, accumulation of gypsum; k, accumulation of secondary carbonates. The meaning of 1450× is magnifying 1450 by microscope. Mg-EG, Mg-ethylene glycol.

(soluble, exchangeable, non-exchangeable and structural), clay minerals (including illite, smectite, vermiculite and smectite+vermiculite) and physical-chemical properties (including CEC, clay, OC and CCE) are given in Table 4.

### 3.3.1 Soluble and exchangeable K

The results in Tables 3 and 4 showed that soluble K varied in pedons, although it was higher in surface soils than in subsurface soils and was significantly correlated with OC and exchangeable K (Pearson correlation coefficients of 0.465 and 0.468, respectively). Soluble K did not show significant correlation with other soil physical-chemical properties (CEC, clay content and CCE), clay minerals (illite, smectite, vermiculite and smectite+vermiculite), and other two K forms (non-exchangeable and structural). Soluble K can be affected by K fertilizers, plant uptake, replacement by other K forms, and sampling time. There are several K minerals in soils, but availability of the K soluble form for plant growth is usually limited (Hayashi et al., 2014). Soluble K was the smallest part of total K in surface and subsurface soils (accounting for 0.1% of total K). In the study area, exchangeable K accounted for 3.3% of total K in surface soils and 2.2% in subsurface soils. Exchangeable K was higher in surface soils than in subsurface soils. The largest amount of exchangeable K in the study area was in surface soils of pedons 36 (Mollisols), 49 (Alfisols), 33 (Alfisols), 46 (Mollisols), 2 (Mollisols) and 39 (Vertisols). In these pedons, OC content was high and smectite was a predominant mineral. In addition, lower amount of exchangeable K was found in subsurface soils of pedons 7 (Alfisols), 29 (Entisols), 53 (Entisols), 13 (Inceptisols), 30 (Inceptisols), 11 (Entisols) and 12 (Inceptisols). These results revealed that poor-developed soils, except pedon 7 due to the presence of Gachsaran formation (palygorskite as

**Table 3** Amounts of different K forms and cumulative non-exchangeable K released in different media of extraction in representative pedons

Pedon	Soluble K		Exchangeable K		Non-exchangeable K		Structural K		Cumulative non-exchangeable K			
									0.01 M CaCl <sub>2</sub>		0.01 M oxalic acid	
	SurS	SubS	SurS	SubS	SurS	SubS	SurS	SubS	SurS	SubS	SurS	SubS
(mg/kg)												
1	2.5	7.0	122	77	280	148	3889	1993	231	183	201	145
2	3.0	0.8	288	161	515	326	6380	5930	276	232	246	217
3	3.4	11.0	251	148	446	365	6001	5988	240	224	220	200
5	1.0	0.4	122	73	251	255	4597	4730	153	144	135	118
7	1.1	0.2	110	27	244	161	3855	3696	147	149	142	131
11	2.7	0.3	155	62	326	175	3727	3809	192	151	171	136
12	3.5	0.7	129	67	329	349	4167	4468	160	135	148	129
13	4.9	2.1	116	44	237	188	4102	4225	157	121	152	113
15	1.9	2.2	110	79	280	168	3818	4896	146	129	134	117
17	36.0	3.3	181	85	266	213	4751	5288	154	169	148	151
21	4.9	1.8	179	73	251	181	5517	4889	157	138	153	132
23	1.4	2.0	104	142	273	155	3668	3111	144	126	129	121
26	2.1	0.3	216	102	405	266	7564	6525	210	167	189	152
29	3.8	0.4	195	39	455	98	5116	2230	166	111	174	117
30	0.9	0.3	116	56	230	175	3458	3414	151	168	153	158
33	6.2	4.8	396	175	699	421	7815	6979	305	214	296	203
34	1.2	0.7	251	85	381	142	6164	2951	257	136	234	139
35	1.4	0.2	244	71	446	251	5538	4391	259	188	243	169
36	28.0	0.9	709	216	690	389	6354	6192	513	215	488	198
38	0.4	0.2	116	157	455	373	6909	7110	236	211	197	165
39	1.2	0.2	273	181	541	489	8314	9328	265	193	–	–
40	0.9	2.9	155	161	405	515	9108	9320	213	215	–	–
42	1.1	0.6	223	116	497	421	6464	7751	243	210	212	173
44	1.4	0.6	195	163	387	532	5277	5440	239	234	209	206
45	2.4	0.8	266	280	303	230	4057	4374	246	231	231	208
46	7.6	2.3	310	295	492	209	5607	7578	261	241	228	221
47	1.1	0.5	104	73	326	148	5338	4663	150	139	131	129
49	2.4	0.5	405	142	680	463	8256	7788	307	203	249	180
51	0.4	1.2	202	438	956	892	8185	10,494	292	344	247	–
52	2.6	3.7	268	199	446	318	5984	5896	298	259	267	231
53	0.7	2.3	98	39	489	80	6598	3524	252	109	233	89
54	1.3	2.6	142	91	389	341	6555	7245	193	145	172	129
Mean	4.2	1.8	211	129	418	295	5723	5507	225	182	204	158

Note: SurS, surface soil; SubS, subsurface soil; –, no data.

the predominant mineral), had less exchangeable K. In these soils, the main minerals were illite, chlorite, and palygorskite. The relationship between different forms of K is generally influenced by the type of clay and soil texture (Nabiollahy et al., 2006). Moreover, exchangeable K is retained by expanding clay minerals (Sharpley, 1989). Bhonsle et al. (1992) reported that the largest amount of exchangeable K is in soils with smectite as the main mineral. Exchangeable K is held throughout electrostatic charges present on organic matter and clay particles (Conyers and McLean, 1969). Enriched sources of illite in the surrounding areas and alteration of biotite in surface soils due to daily and seasonal variations of moisture and temperature resulted in illite decreased with increasing soil depth (Khormali and Abtahi, 2003). Alteration of illite to smectite occurred in surface soils of Alfisols and other soils in humid regions. Compared to illite, smectite

can be transformed and deposited into subsurface soils because smectite is in fine fraction, but the major reason could be due to the presence of a lot of smectite in parent materials which increases with increasing soil depth.

Exchangeable K was significantly correlated with OC, CEC, CCE, illite, smectite and vermiculite (Pearson correlation coefficients of 0.784, 0.663, -0.474, 0.293, 0.263 and 0.313, respectively; Table 4). Due to more smectite and high OC content in surface soils, the amount of exchangeable K in surface soils was higher than that in subsurface soils. The high correlations of exchangeable K with OC and CEC referred especially to the organic matter and clay surface, which are able to absorb and exchange K in soils. It seems that organic matter plays a more important role than smectite mineral in retaining exchangeable K in the studied soils. Raheb and Heidari (2012) stated that the smectitic soils are rich in exchangeable K, whereas the predominant illite soils exhibit low amount of exchangeable K. In addition, there are significant correlations of exchangeable K with CEC and OC.

**Table 4** Pearson correlation coefficients between soil K forms, clay minerals and physical-chemical properties

	Sol	Exc	Non-exc	Str	CEC	OC	Clay	CCE	Ill	Sme	Ver
Exc	0.468**										
Non-exc	0.135	0.476**									
Str	0.024	0.321*	0.757**								
CEC	0.074	0.663**	0.441**	0.543**							
OC	0.465**	0.784**	0.277*	0.163	0.580**						
Clay	-0.223	0.218	0.290*	0.506**	0.612**	0.097					
CCE	0.111	-0.474**	-0.447**	-0.572**	-0.776**	-0.361**	-0.557**				
Ill	-0.061	0.293*	0.361**	0.301*	0.362**	0.153	0.512**	-0.472**			
Sme	-0.191	0.263*	0.324*	0.552**	0.672**	0.058	0.770**	-0.466**	0.264*		
Ver	-0.151	0.313*	0.373**	0.509**	0.696**	0.153	0.580**	-0.506**	0.329*	0.754**	
Sme+Ver	-0.187	0.299*	0.364**	0.569**	0.724**	0.099	0.743**	-0.512**	0.307*	0.965**	0.900**

Note: \*, significance at  $P < 0.05$  level; \*\*, significance at  $P < 0.01$  level. Sol, soluble K; Exc, exchangeable K; Non-exc, non-exchangeable K; Str, structural K; CEC, cation exchangeable capacity; OC, organic carbon; CCE, calcium carbonate equivalent; Ill, illite; Sme, smectite; Ver, vermiculite.

### 3.3.2 Non-exchangeable and structural K

Non-exchangeable K can be calculated through subtraction of exchangeable K extracted by 1 M  $\text{NH}_4\text{OAc}$  solution from the experimental amount of extractable K by nitric acid. Non-exchangeable K is different from structural (mineral) K. This form of K, against the structural K, is trapped in the tetrahedral layers of 2:1 minerals such as illite and vermiculite (Sparks, 2000). Similar to exchangeable K, the non-exchangeable K in the study area was also higher in surface soils than in subsurface soils and was significantly correlated with illite (Pearson correlation coefficient of 0.361), vermiculite (0.373), smectite (0.324), clay content (0.290), CEC (0.441), OC (0.277) and CCE (-0.447) (Table 4). Raheb and Heidari (2012) found that due to the thermal and moisture conditions for weathering of primary minerals, the exchangeable and non-exchangeable K contents in surface soils were higher than those in subsurface soils. In the study area, some representative pedons such as 51 (Alfisols), 33 (Alfisols), 36 (Molisols), 49 (Alfisols) and 39 (Vertisols) had the larger amount of non-exchangeable K in surface soils (956, 699, 690, 680 and 541 mg/kg, respectively) and subsurface soils (892, 421, 389, 463 and 541 mg/kg, respectively), while subsurface soils in the Entisols including pedons 53, 29, 34 and 47 had the lower amounts of non-exchangeable K. Alfisols in semi-arid regions are the most well-developed soils with moderate leaching. In the study area, Alfisols were the dominant soils because of high precipitation in the north and east in the present and past. High precipitation in these regions (northern and eastern parts) caused the leaching of  $\text{CaCO}_3$  from soil solum. Due to the enriched sources of  $\text{CaCO}_3$  from the surrounding areas (calcareous geology formations with more than 90%  $\text{CaCO}_3$ ),  $\text{CaCO}_3$  is added to soils in the study area recurrently. Consequently, low amount of vermiculite was found in the study area especially in surface soils, as well as moderate

amount of illite, which is suggested to be due to water and wind erosion sediments from the surrounding mountains. Furthermore, high amount of smectite was found in the regions with high precipitation. The  $\text{CaCO}_3$  equivalent is an important influencing factor on the K forms. High significant negative correlation between CCE and non-exchangeable K revealed that a decrease in  $\text{CaCO}_3$  could cause increases in clay content and clay minerals. High clay content, smectites with different layer charges, and the presence of illite and vermiculite as large reserves of K are the reasons for the large amount of non-exchangeable K in these soils. This is consistent with the findings of Najafi Ghiri et al. (2010), who concluded that the amount of non-exchangeable K in soils with smectite as the mainly mineral is higher than that in soils with palygorskite and chlorite as the main minerals. Also, Hashemi and Abbaslou (2016) observed a significant correlation between non-exchangeable K and illite mineral in calcareous soils. Schindler et al. (2003) and Komadel et al. (2006) reported that the change of dioctahedral  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  contributes to the increase in K fixation in smectitic phyllosilicates. As a matter of fact, the strong interlayer forces, which ultimately result from  $\text{Fe}^{3+}$  reduction, may lead to layer collapses and thus trap interlayer cations such as  $\text{K}^+$ . Low clay content, high CCE, poor-developed soil, and the presence of a large quantity of minerals containing less K like palygorskite, resulted in the small quantity of K in subsurface of Entisols in the study area. Zhan et al. (2014) stated that the differences of K fixation capacity in different soils may be related to the physical-chemical properties of soils such as CEC, clay content,  $\text{K}^+$  saturation, and soil K content. Hosseinpour and Sinegani (2007) pointed out that the soils with heavy texture (clayey) and the soils with smectite as the predominant clay mineral have the largest quantity of non-exchangeable K. The soils with 2:1 clay minerals such as high-layer-charge smectite, vermiculite and illite, contain larger quantity of non-exchangeable K than the soils with kaolinite as the main mineral (Ghosh and Singh, 2001).

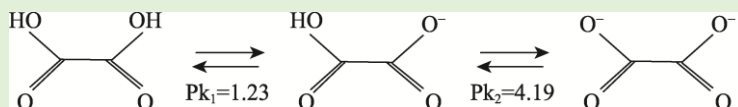
In the study area, structural K in surface and subsurface soils accounted for 90.0% and 92.8% of total K, respectively. It seems that these values may result from the fact that suitable conditions like temperature and humidity in surface soils for weathering cause more K to be released from primary and secondary minerals than the subsurface soils. Consequently, transformation in K reserve and translocation into deep soil depth contribute to less structural K in surface soils. Regarding parent rock and stage of soil development, structural K can constitute up to about 98% of total K in soils (Sparks and Huang, 1985). In the study area, pedons containing high structural K including 51 (Alfisols), 39 (Vertisols), 40 (Inceptisols), 49 (Alfisols), 42 (Alfisols) and 46 (Mollisols) are located in regions with high humidity. As shown in Table 4, structural K was significantly correlated with non-exchangeable K (Pearson correlation coefficient of 0.757), exchangeable K (0.321), CEC (0.543), clay content (0.506), CCE (−0.572), illite (0.301), smectite (0.552), vermiculite (0.509) and smectite+vermiculite (0.569). These results revealed that vermiculite, high-layer-charge smectite and illite play important roles in the high amount of structural K. Significant negative correlation of CCE with structural K in humid regions (pointed in non-exchangeable K) resulted in increases of clay content and clay minerals in soils. Although the amount of illite was the same in almost all pedons in the study area, structural K was higher in humid regions than in arid and semi-arid regions. This difference may be related to the poor reservoir of  $\text{K}^+$  minerals like palygorskite and chlorite accompanied by illite in arid and semi-arid regions. In humid regions, illite was accompanied by vermiculite and smectite as the  $\text{K}^+$  reservoir.

### 3.4 K released from clay minerals by $\text{CaCl}_2$ and oxalic acid

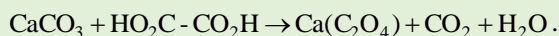
In this study, we evaluated the K released from clay minerals to calculate the amount of non-exchangeable K that can be released. Although non-exchangeable K is fixed, it can be released when exchangeable and soluble K is reduced through plant uptake or leaching. In calcareous soils,  $\text{Ca}^{2+}$  can be replaced by  $\text{K}^+$  easier than others due to high quantity of  $\text{Ca}^{2+}$  in soil solution (Jalali, 2006). Also, K is weakly maintained compared to  $\text{Ca}^{2+}$ , therefore K is more readily exchangeable than  $\text{Ca}^{2+}$  (Zhang et al., 2015). Oxalic acid is exuded by plant roots and causes weathering of minerals and K release. As the results, the mean amounts of non-exchangeable  $\text{K}^+$  released from surface soils by 0.01 M  $\text{CaCl}_2$  and 0.01 M oxalic acid were higher than those released from subsurface soils (Table 3). Specifically, 225 mg/kg



non-exchangeable K was released from surface soils by  $\text{CaCl}_2$  and 182 mg/kg non-exchangeable K was released from subsurface soils by  $\text{CaCl}_2$ ; while 204 mg/kg non-exchangeable K was released from surface soils by oxalic acid and 158 mg/kg non-exchangeable K was released from subsurface soils by oxalic acid. Mean cumulative non-exchangeable K released by  $\text{CaCl}_2$  was higher than that released by oxalic acid. Oxalic acid can release K in soils by replacement or mineral destruction. Oxalic acid can be ionized as follows:



One  $\text{H}^+$  ion and two  $\text{H}^+$  ions are removed from oxalic acid at  $\text{pH}=3.5$  and  $\text{pH}>4.5$ , respectively. In the study area, average soil  $\text{pH}$  is about 7.8 and oxalic acid separates to oxalate and  $\text{H}^+$  ions. In calcareous soils, there are abundant  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions, so when oxalic acid is added to calcareous soils (the reaction function below), the  $\text{OH}^-$  ions in soil solution are neutralized by the  $\text{H}^+$  ions liberated by the oxalic acid. Also, the reaction between oxalate and  $\text{Ca}^{2+}$  ions can produce calcium oxalate as an insoluble salt.



Tu et al. (2007) and Wani (2012) reported that soils with mica and smectite as main minerals as well as calcareous soils could release less K due to high buffering capacity of soils. Opposite results were also obtained. For example, Jalali and Zarabi (2006) reported that oxalic acid could release more non-exchangeable K than  $\text{CaCl}_2$  in some soils. It seems that in their experiments, less  $\text{CaCO}_3$  is responsible for more K release when oxalic acid is added.

## 4 Conclusions

The results showed that soils in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran were classified into 5 orders including Entisols, Inceptisols, Mollisols, Alfisols and Vertisols, of which smectite, chlorite, illite, palygorskite, vermiculite, kaolinite and interstratified illite-smectite were the dominant clay minerals in its clay fraction. The main clay minerals were illite, chlorite and palygorskite in the west and south of Kohgiluyeh and Boyer-Ahmad Province, whereas they were smectite, vermiculite and illite in the north and east of the province. Since a decrease in  $\text{CaCO}_3$  could result in increases of clay content and clay minerals, there was significant negative correlations of CCE with exchangeable, non-exchangeable, and structural K. In contrast to structural K, exchangeable and non-exchangeable K amounts in surface soils were higher than those in subsurface soils. It seems that organic matter plays a more important role than smectite mineral in retaining exchangeable K in the studied soils. Non-exchangeable K showed close relationships with illite, vermiculite, smectite, clay content, CEC, OC and CCE. In the study area, some representative pedons that occurred in region with high precipitation such as 51 (Alfisols), 33 (Alfisols), 36 (Mollisols), 49 (Alfisols) and 39 (Vertisols) had the higher amount of non-exchangeable K in surface and subsurface soils, while subsurface soils in Entisols including pedons 53, 29, 34 and 47 had the lower amount of non-exchangeable K. High clay content, smectites with different layer charges and the presence of illite and vermiculite as large reserves of K are the reasons for the high amount of non-exchangeable K in these soils. The quantity of structural K as a K reserve was depended on vermiculite, high-layer-charge smectite and illite. Structural and non-exchangeable K amounts were higher in humid regions than in arid and semi-arid regions. Mean cumulative non-exchangeable K released by  $\text{CaCl}_2$  was higher than that released by Oxalic acid. This study could provide a scientific reference to reduce K loss and obtain high crop production in agricultural lands in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran.

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